



## What does the global mean OH concentration tell us?

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**Global mean OH  
concentration**

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# What does the global mean OH concentration tell us?

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## Abstract

The global mean OH concentration ( $[\text{OH}]_{\text{GM}}$ ) has been used as an indicator of the atmospheric oxidizing efficiency or its changes over time. It is also used for evaluating the performance of atmospheric chemistry models by comparing with other models or with observationally-based reference  $[\text{OH}]_{\text{GM}}$  levels. We contend that the treatment of this quantity in the recent literature renders it problematic for either of these purposes. Several different methods have historically been used to compute  $[\text{OH}]_{\text{GM}}$ : weighting by atmospheric mass or volume, or by the reaction with  $\text{CH}_4$  or  $\text{CH}_3\text{CCl}_3$ . In addition, these have been applied over different domains to represent the troposphere. While it is clear that this can lead to inconsistent  $[\text{OH}]_{\text{GM}}$  values, to date there has been no careful assessment of the differences expected when  $[\text{OH}]_{\text{GM}}$  is computed using various weightings and domains. Here these differences are considered using four different 3D OH distributions, along with the weightings mentioned above applied over various atmospheric domains. We find that the  $[\text{OH}]_{\text{GM}}$  values computed based on a given distribution but using different domains for the troposphere can result in differences of 10% or more, while different weightings can lead to differences of up to 30%, comparable to the uncertainty which is commonly stated for  $[\text{OH}]_{\text{GM}}$  or its trend. Thus, at present comparing  $[\text{OH}]_{\text{GM}}$  values or trends from different studies does not provide clearly interpretable information about whether the OH amounts are actually similar or not, except in the few cases where the same weighting and domain have been used in both studies. Furthermore, we find that the only direct indicator of the global atmospheric oxidizing efficiency of OH with respect to a particular gas (e.g.  $\text{CH}_4$  or  $\text{CH}_3\text{CCl}_3$ ) is the  $[\text{OH}]_{\text{GM}}$  value weighted by the reaction with that gas; the mass-weighted and volume-weighted  $[\text{OH}]_{\text{GM}}$  values, in contrast, are generally poor indicators of the atmospheric oxidizing efficiency on a global basis (regionally they are better). We recommend that in future studies the  $[\text{OH}]_{\text{GM}}$  value weighted by the reaction with  $\text{CH}_4$ , along with the  $\text{CH}_4$  turnover time, be given as the primary indicators of the atmospheric oxidizing efficiency, and that serious evaluations of modeled OH

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concentrations be done with air mass weighted  $[\text{OH}]_{\text{GM}}$  broken down into atmospheric sub-compartments, especially focusing on the tropics, where the atmospheric oxidizing efficiency is greatest.

## 1. Introduction

5 The hydroxyl radical, OH, plays a critical role in the chemistry of the earth's troposphere. The earliest recognition of its importance came over three decades ago (Levy, 1971), and since then has grown considerably. OH is responsible for most of the breakdown of  $\text{CH}_4$  and CO, particularly in the tropics (Crutzen and Zimmermann, 1991; Crutzen et al., 1999), and initiates the breakdown of most non-methane hydrocarbons (NMHCs) (e.g. Atkinson, 2000). When these oxidation chains occur in the presence of sufficient levels of nitrogen oxides, photochemical production of  $\text{O}_3$  results (Crutzen, 1972, 1973, 1974; Chameides and Walker, 1973). OH also provides one of the major gas phase reaction pathways for  $\text{SO}_2$  and dimethylsulfide (e.g. Yin et al., 1990), and thereby influences the atmospheric sulphur cycle, as well as aerosol and cloud particle formation (e.g. Kiehl et al., 2000). Likewise, it is a major factor in the removal of reactive nitrogen, via reaction of OH with  $\text{NO}_2$  to form the highly soluble gas  $\text{HNO}_3$ , which is readily removed by precipitation (Crutzen and Lawrence, 2000). While other reactive gases, in particular Cl,  $\text{NO}_3$ , and  $\text{O}_3$ , can play important secondary roles, OH stands out as the most important oxidant in the troposphere.

20 Because of its primary role in initiating atmospheric oxidation chains, the global mean OH level,  $[\text{OH}]_{\text{GM}}$ , has been used as a metric for the atmospheric oxidizing efficiency. There are various possible definitions of the oxidizing efficiency. For the purposes of this study, it will be defined as the rate of removal of a gas from some atmospheric domain relative to the amount of the gas in that domain; this is equivalent to the inverse of the "turnover time" or "(static) lifetime" of the trace gas.

25 Ideally, then,  $[\text{OH}]_{\text{GM}}$  should have some consistent relationship to the turnover time of a given gas in order to be a good indicator of the oxidizing efficiency with respect to

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that particular gas. There are several different ways to compute  $[\text{OH}]_{GM}$ , for instance, weighting by atmospheric mass or volume, or by the reaction with long-lived tracers such as methane ( $\text{CH}_4$ ) and methylchloroform ( $\text{CH}_3\text{CCl}_3$ , or “MCF”). These various techniques can yield very different values of  $[\text{OH}]_{GM}$ . To illustrate this, consider the extreme example of two OH distributions with the same total number of OH molecules in the troposphere, but where one has OH concentrated mainly in the tropics, while the other has the most OH in the extratropics. These two OH distributions will have the same volume-weighted  $[\text{OH}]_{GM}$  values. However, since reaction rates are generally temperature dependent, they will have very different  $[\text{OH}]_{GM}$  values if they are instead calculated by weighting with the reaction rate of  $\text{CH}_4$  or  $\text{CH}_3\text{CCl}_3$ , and will also clearly result in different turnover times of these gases. Similarly, the domain considered, particularly the vertical extent defining the troposphere, can also influence the relationship between  $[\text{OH}]_{GM}$  and the tropospheric oxidizing efficiency. For instance, since OH is usually less concentrated in the upper troposphere than lower down, integrating from the surface to 100 hPa versus only integrating to 200 hPa can lead to notable changes in the mass- and volume-weighted  $[\text{OH}]_{GM}$  values, as well as in trace gas turnover times.

In a brief survey of recent literature, we have found that a wide variety of weightings and domains have been employed to compute  $[\text{OH}]_{GM}$ ; the survey results are summarized in Table 1 (the authors welcome further information about  $[\text{OH}]_{GM}$  values published since 1990 which are not included in this table, as well as information on the weightings/domains which have been used). Table 1, along with the values to be discussed later in Table 2, provides the most extensive comparison of recent published  $[\text{OH}]_{GM}$  values of which we are aware. There are several factors which lead to the wide range of numbers in Table 1, and which make them difficult to compare. First, different techniques are used to compute the global OH distribution on which  $[\text{OH}]_{GM}$  is based, for instance, using a 3D chemistry-transport model, using kinetic box models constrained by observations of key parameters (e.g.  $\text{O}_3$ ,  $\text{CO}$ ), and using the inferred loss rate of  $\text{CH}_3\text{CCl}_3$  based on its emissions, distribution and trend. Second, the basic

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parameters which are used in each of these techniques, such as reaction rates, photolysis rates, and the calibration of  $\text{CH}_3\text{CCl}_3$  measurements, are subject to change over time (in particular, the latter parameter changed notably in the mid-1990's). Finally, the weightings and domains chosen to compute  $[\text{OH}]_{\text{GM}}$  will influence the results. This study focuses on determining the magnitude of influence of the latter factor; the first two issues will need to be considered in future studies which are concerned with global OH.

Nearly every study listed in Table 1 uses a different combination of weighting and domain for computing  $[\text{OH}]_{\text{GM}}$ . The four main weighting factors which have been used are atmospheric mass, volume, and the reactions with  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$ ; others, for instance  $\text{CH}_3\text{CCl}_3$  mass (Prinn et al., 1995, 2001), have also been used. The domain is usually either the 100 hPa or 200 hPa pressure level, or some sort of latitudinally dependent tropopause, though other domains have also been used. Nevertheless, despite the potential differences pointed out in the example above, the manner in which  $[\text{OH}]_{\text{GM}}$  was computed is not always clear: out of 18 papers, only about half stated clearly how  $[\text{OH}]_{\text{GM}}$  was weighted, while in the rest this information either could not be found, or was not completely clear (note that for several of these, the weighting which was actually used was determined by personal communication with the authors). This has occurred despite the fact that (Prather and Spivakovsky, 1990) pointed out that “it is misleading to report a single ‘global average OH concentration ( $\langle\text{OH}\rangle$ )’ without qualifying it as to the averaging kernel”. It is interesting to note that the weighting used is more frequently stated in recent papers than in older papers, and that some of the most recent studies also give  $[\text{OH}]_{\text{GM}}$  values for more than one method of computation (Prinn et al., 2001; Spivakovsky et al., 2000; Poisson et al., 2000; Wang et al., 1998).

Given this wide variety of weightings and domains, a direct interpretation of the results would be difficult. The comparability of these numbers depends on exactly how much of a difference it makes when different weightings and domains are applied when calculating  $[\text{OH}]_{\text{GM}}$ . The illustrations given above make it clear that large differences are certainly possible; the more crucial question is: are the differences likely to be sig-

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nificant in light of other uncertainties in computing  $[\text{OH}]_{GM}$ , given what we know about the global OH distribution? We examine this question here from the perspective of understanding what the global mean OH concentration tells us about the atmospheric oxidizing efficiency, and how we can best go about comparing OH levels with this in mind. To do so, we consider  $[\text{OH}]_{GM}$  computed based on four 3D OH distributions, using several of the various weightings and domains encountered in Table 1. The four OH distributions chosen for this study are described in the next section; they can be considered representative of the range of characteristic distributions found in the recent literature. In Section 3, we discuss the various techniques used to compute  $[\text{OH}]_{GM}$ , and the physical interpretation of each of these, in particular their relationship to trace gas turnover times. Section 4 considers the influence of different weighting factors on  $[\text{OH}]_{GM}$  values computed for the four distributions; Sect. 5 considers the same for different domains. Sections 6 and 7 examine the regional distribution of  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  oxidation in the troposphere, and how this can be used to help choose a set of subdomains appropriate for future comparisons of OH distributions. Section 8 gives our conclusions and recommendations for future studies.

## 2. OH fields description

We examine  $[\text{OH}]_{GM}$  using four different global OH distributions. The first one, OH-S, is from the empirical analysis of (Spivakovsky et al., 2000), which gives the OH distribution on an  $8^\circ \times 10^\circ$  grid in pressure intervals of 100 hPa. Their OH levels are computed based on a photochemical box model combined with observed distributions of the main parameters influencing local OH, e.g.  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{NO}_x$ , hydrocarbons, and solar radiation. The other three global OH distributions used here, OH-1, OH-2, and OH-3, were computed using the global 3D chemistry-transport model MATCH (Model of Atmospheric Transport and Chemistry; (Rasch et al., 1997), in its extended configuration MATCH-MPIC (Max-Planck-Institute for Chemistry version), which includes tropospheric chemistry; output from three different versions are used here (OH-1 is

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from MATCH-MPIC 1.2, (Lawrence, 1996); OH-2 is from MATCH-MPIC 2.0, (Lawrence et al., 1999); OH-3 is from MATCH-MPIC 3.0, (von Kuhlmann, 2001)). All three of these were computed at a relatively high horizontal resolution of about  $2 \times 2$  degrees (T63), with 28 sigma levels between the surface and about 2 hPa. An extensive discussion of the testing of three of these distributions (all but OH-3) using various tracers such as  $\text{CH}_3\text{CCl}_3$  and  $^{14}\text{CO}$  is given by (Jöckel, 2000). There were numerous differences between the three MATCH-MPIC model versions, in particular the inclusion of non-methane hydrocarbon reactions in computing OH-3 (OH-1 and OH-2 are based on  $\text{CH}_4$ -only chemistry), along with other major modifications, such as the advection and convection schemes, several emissions fields, and a few key reaction rates, resulting in rather different OH fields (see (Lawrence et al., 1999) and (von Kuhlmann, 2001) for more details).

The annual zonal mean OH levels based on these four distributions are shown in Fig. 1; these and all values discussed here are day and night (24-hour) means, rather than daytime-only means (OH concentrations are very low at night compared to day). OH-S is largely hemispherically symmetric, while OH-1, OH-2, and OH-3 have notably more OH in the northern hemisphere. OH-S, OH-1, and OH-3 have the highest zonal mean OH levels in the tropical mid-troposphere, peaking at about  $2.3 \times 10^6$  molec/cm<sup>3</sup> in both, at a somewhat higher altitude (600 hPa) in OH-S and OH-1 than in OH-3 (700 hPa). The OH-2 distribution has a maximum much closer to the surface, and the peak value is lower, around  $1.8 \times 10^6$  molec/cm<sup>3</sup>. The OH-2 distribution resembles another recent study focused on global OH (Krol et al., 1998), while some other models (e.g. Crutzen and Zimmermann, 1991; Wang et al., 1998) compute OH distributions which more closely resemble the OH-S distribution. Although we focus mainly on vertical differences here, there are also important horizontal differences; in particular, OH is depleted over the forested tropical continents in the OH-3 and OH-S distributions, due to the influence of isoprene and other NMHCs on OH in source regions, in contrast to OH-1 and OH-2 (which do not include the effects of NMHCs).

These four distributions are used in this study in an effort to represent much of the

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range of recent estimates of the global OH distribution, although some models predict distributions which are quite different than these (e.g. with OH concentrations maximizing in the upper troposphere, (Collins et al., 1997)). Furthermore, other differences are possible, in particular over the oceans, where ship emissions of NO may or may not enhance the OH concentration (Lawrence and Crutzen, 1999; Kashibhatla et al., 2000), and in the upper troposphere, where the convective supply of HO<sub>x</sub> precursors is still rather uncertain (e.g. Jaeglé et al., 2001).

### 3. Computing the global mean OH concentration

[OH]<sub>GM</sub> is generally computed from a 2D or 3D OH distribution by applying some type of weighting factor, W:

$$[\text{OH}]_{GM} = \frac{\Sigma(W \cdot [\text{OH}])}{\Sigma W}, \quad (1)$$

where the summation is over all grid cells in a chosen region (e.g. the troposphere). The weighting factor W can take on different forms. Often either the air mass or the air volume are used. The volume-weighted variant (hereafter ([OH]<sub>GM</sub>(V)) is the literal interpretation of a global mean concentration: all OH molecules spread over the total volume of the troposphere. We therefore assume it is likely that some of the studies in Table 1 which did not state the weighting used were adopting this literal definition, and thus considered it to be superfluous to specify how [OH]<sub>GM</sub> was computed. It is difficult, however, to assign a physical meaning to this parameter in terms of other relevant atmospheric quantities. The mass-weighted value (hereafter [OH]<sub>GM</sub>(M)) can be considered as indicative of the oxidizing efficiency (or turnover time) for a uniformly-distributed gas with no temperature or pressure dependence in its reaction with OH (see Equations 2–5 below).

Alternatively, W can be chosen to provide information about the turnover time of a given gas X, in which case the global mean OH concentration (hereafter [OH]<sub>GM</sub>(X))

is computed using:

$$W = k_X(T, P) \cdot M_X \quad (2)$$

where  $k_X$  is the reaction rate of OH with the gas X, usually temperature and/or pressure dependent, and  $M_X$  is the mass of the gas in a grid cell. X is generally chosen to be a long-lived gas which primarily reacts with OH, in particular  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$ . It is occasionally assumed that the distribution of some long-lived gases such as  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  can be treated as uniformly distributed (e.g. [Spivakovsky et al., 2000](#)), so that an alternative weighting would be  $W = k_X(T, P) \cdot M_{\text{air}}$ , where  $M_{\text{air}}$  is the air mass. For the cases considered here, this assumption is generally very good, and leads to <1% error in the annual mean  $[\text{OH}]_{GM}$  values (<5% for monthly values), compared to using  $M_X$  in Eq. 2.

In this study, we consider  $[\text{OH}]_{GM}$  for four distinct weightings: air mass ( $[\text{OH}]_{GM}(\text{M})$ ); volume ( $[\text{OH}]_{GM}(\text{V})$ ); and reaction with  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  ( $[\text{OH}]_{GM}(\text{CH}_4)$  and  $[\text{OH}]_{GM}(\text{MCF})$ , respectively). For the temperature, air mass, and tracer mass fields ( $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$ ) which are needed for these calculations, we employed the distributions from MATCH-MPIC version 2.0 (for  $\text{CH}_4$ , see [Lawrence et al., 1999](#); for  $\text{CH}_3\text{CCl}_3$ , see [Jöckel, 2000](#)); note that we also tested using the fields from an earlier model version (MATCH-MPIC 1.2), and obtained essentially the same results.

As discussed in the introduction, we define the atmospheric oxidizing efficiency with respect to a given gas X to be the inverse of the turnover time ( $\tau(X)$ ), also commonly referred to as the “lifetime”) of that gas, where:

$$\tau(X) = \frac{\Sigma M_X}{\Sigma(k_X \cdot [\text{OH}] \cdot M_X)} \quad (3)$$

Combining this with equations (1) and (2) for the reaction rate weighted mean OH ( $[\text{OH}]_{GM}(X)$ ) yields:

$$\tau(X) = \alpha \cdot ([\text{OH}]_{GM}(X))^{-1} \quad (4)$$

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where

$$\alpha = \frac{\Sigma M_X}{\Sigma(k_X \cdot M_X)} \quad (5)$$

Thus, for a well-mixed gas,  $\tau(X)$  and  $[\text{OH}]_{GM}(X)$  are inversely related by the coefficient  $\alpha$ , whose value generally depends only on the temperature distribution in the atmosphere (and the domain over which the summation is applied). For the  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  distributions and reaction rates used here, integrated over the climatological troposphere domain defined below (Eq. 6),  $\alpha$  (in  $\text{yr} \cdot \text{molec}/\text{cm}^3$ ) is computed to be 10.86 and 6.41, respectively. The same values (within roundoff) are computed assuming the gases are uniformly distributed. However, integrating over different domains results in considerably different values: below 300 hPa yields 9.54 and 5.71, below 200 hPa yields 10.47 and 6.20, and below 100 hPa yields 11.48 and 6.69. This is due to two factors. First, the  $[\text{OH}]_{GM}(\text{CH}_4)$  and  $[\text{OH}]_{GM}(\text{MCF})$  values do not change much for different vertical domains, since the amount which reacts with  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  in the upper troposphere is minimal (see Sect. 6), so that the UT is only weighted weakly. On the other hand, the turnover time is strongly dependent on the vertical extent over which it is computed; for example, extending the upper bound to a higher altitude does not add much to the total loss (in  $\text{Tg}/\text{yr}$ ), but it does add to the tracer mass (in  $\text{Tg}$ ). Thus, since in Eq. (4)  $[\text{OH}]_{GM}(X)$  is relatively constant with altitude, whereas  $\tau(X)$  varies notably,  $\alpha$  must also vary strongly with the extent of the tropospheric domain.

#### 4. Influence of the weighting factor on $[\text{OH}]_{GM}$

In this section the differences in  $[\text{OH}]_{GM}$  values due to using different weightings will be discussed.  $[\text{OH}]_{GM}$  based on the OH distributions and weightings discussed above are given in Table 2 and Fig. 2. For reference, the implied turnover times for  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  are also listed (Table 3). Monthly mean fields (OH,  $\text{CH}_4$ , etc.) were used in these computations, and then averaged to yield annual means. Only the annual mean

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results are discussed here; values for individual months lead to the same conclusions as the annual means. In this section, results are only considered for the domain below a climatological tropopause, defined as

$$p > 300 - 215(\cos(\phi))^2 \quad (6)$$

5 where  $p$  is the pressure in hPa (see (Jöckel, 2000), for further discussion of this tropopause definition); differences due to the definition of the tropospheric domain are considered in the next section.

The spread ((maximum-minimum)/average) in  $[\text{OH}]_{GM}$  calculated using the different weightings is about 18% for OH-S, 10% for OH-1, 25% for OH-2, and 31% for OH-3, comparable to or larger than the uncertainty ranges in  $[\text{OH}]_{GM}$  stated by (Spivakovsky et al., 2000), (Krol et al., 1998), and (Prinn et al., 1995, 2001). The results indicate that weighting by the reaction with  $\text{CH}_4$  or  $\text{CH}_3\text{CCl}_3$  always yields the highest values for  $[\text{OH}]_{GM}$ . This is due to the strong temperature dependence of these reactions, so that the tropics and the mid to lower troposphere, where OH concentrations are highest (Fig. 1), are weighted most strongly.  $[\text{OH}]_{GM}(\text{M})$  and  $[\text{OH}]_{GM}(\text{V})$  are generally closer to each other than to  $[\text{OH}]_{GM}(\text{CH}_4)$  and  $[\text{OH}]_{GM}(\text{MCF})$ , though the relationship between the parameters is rather variable. The differences are smallest for OH-1, which is most evenly distributed in the vertical throughout the troposphere (Fig. 1). The other distributions, with OH falling off sharply in the tropical upper troposphere, show larger differences between the four different  $[\text{OH}]_{GM}$  values, especially OH-2, which is weighted most strongly towards the surface, and OH-3, which falls off at lower altitudes in the tropics than the other distributions.

Figure 2b shows the ratio of  $[\text{OH}]_{GM}(\text{M})$ ,  $[\text{OH}]_{GM}(\text{V})$  and  $[\text{OH}]_{GM}(\text{MCF})$  to  $[\text{OH}]_{GM}(\text{CH}_4)$  for each of the four OH distributions. Recall that  $[\text{OH}]_{GM}(\text{CH}_4)$  is directly related to the inverse of  $\tau(\text{CH}_4)$  (Eq. 5), and thus to the atmospheric oxidizing efficiency. In order for any of the other three parameters to also serve as a good indicator of the oxidizing efficiency with respect to  $\text{CH}_4$  which is applicable to any “typical” OH distribution, then they should have a consistent relationship to  $[\text{OH}]_{GM}(\text{CH}_4)$ , i.e. they

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should yield approximately horizontal lines on Fig. 2b. While  $[\text{OH}]_{GM}(\text{MCF})$  essentially fulfills this criterion, the two “generic” parameters  $[\text{OH}]_{GM}(\text{M})$  and  $[\text{OH}]_{GM}(\text{V})$  clearly do not. The ratio between  $[\text{OH}]_{GM}(\text{M})$  and  $[\text{OH}]_{GM}(\text{CH}_4)$  differs by  $>10\%$ , while for  $[\text{OH}]_{GM}(\text{V})$  the ratio varies by  $>20\%$ .

5 Although the principle behind the result in Fig. 2b is clear, since the relationship between OH amounts and the oxidizing efficiency depends on the geographical distribution of OH, to date it has not been made clear how much the relationship between  $[\text{OH}]_{GM}(\text{M})$ ,  $[\text{OH}]_{GM}(\text{V})$  and  $[\text{OH}]_{GM}(\text{CH}_4)$  (or  $\tau(\text{CH}_4)$ ) should actually vary for current estimates of the OH distribution. Based on Fig. 2b we conclude that  $[\text{OH}]_{GM}(\text{M})$  and   
10  $[\text{OH}]_{GM}(\text{V})$  are not very good indicators of the atmospheric oxidizing efficiency, at least not on a global basis. However, when the atmosphere is broken down into smaller domains, over which the temperature and OH concentration do not vary as much, then the ability of the mass- and volume- weighted regional mean OH values to represent the regional oxidation efficiency improves considerably, as discussed in Sect. 7.

## 15 5. Influence of the tropospheric domain on $[\text{OH}]_{GM}$

In this section, the differences in  $[\text{OH}]_{GM}$  computed over four different domains are considered: (1) the region below the climatological tropopause defined in Eq 6, (2) the region below 100 hPa, (3) the region below 200 hPa, and (4) the region below 300 hPa. The first three represent the extremes of what is encountered in Table 1, while   
20 the latter is included because it is purely tropospheric, and contains the region where atmospheric gases like  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  are mainly oxidized (discussed in the next section).

The ratios of  $[\text{OH}]_{GM}(\text{M})$ ,  $[\text{OH}]_{GM}(\text{V})$ ,  $\tau(\text{CH}_4)$ , and  $\tau(\text{CH}_3\text{CCl}_3)$  for the latter three domains versus the values for the climatological troposphere are depicted in Fig. 3,   
25 which shows that the volume-weighted OH values are particularly strongly affected by the chosen domain, varying by 20% or more for the region below 100 hPa versus that below 300 hPa. The turnover times of  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  are almost as strongly af-

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fects, also varying by nearly 20%, while  $[\text{OH}]_{GM}(\text{M})$  varies by about 10%. Restricting this to only the domains encountered in Table 1 (i.e. all but Fig. 3c), the differences are about 10% for  $[\text{OH}]_{GM}(\text{V})$ ,  $\tau(\text{CH}_4)$ , and  $\tau(\text{CH}_3\text{CCl}_3)$ , and about 5% for  $[\text{OH}]_{GM}(\text{M})$ . The OH distribution which shows the least sensitivity to domain is OH-1, due to the relatively high tropical OH values extending vertically to about the 100 hPa level. In contrast, the variation in  $\tau(\text{CH}_4)$  and  $\tau(\text{CH}_3\text{CCl}_3)$  is similar for all four OH distributions, since the amount of tracer which is oxidized in the upper troposphere mainly depends on the rapidly falling temperature, rather than the OH values. On a similar note, the ratios of values for  $[\text{OH}]_{GM}(\text{CH}_4)$  and  $[\text{OH}]_{GM}(\text{MCF})$  are not shown in the figure, since they are all in the range 0.99–1.02. The reason for the weak dependence of these quantities on the chosen tropospheric domain, as discussed previously, is that very little oxidation of  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  occurs in the upper troposphere, and thus the values in the region above 300 hPa are hardly weighted in computing  $[\text{OH}]_{GM}(\text{CH}_4)$  and  $[\text{OH}]_{GM}(\text{MCF})$ . This issue is considered further in the next section.

## 6. The distribution of $\text{CH}_4$ and $\text{CH}_3\text{CCl}_3$ oxidation in the troposphere

It has been well established in previous studies that  $\text{CH}_4$  oxidation is weighted towards the tropics (e.g. Crutzen and Zimmermann, 1991; Crutzen et al., 1999); however, the vertical distribution of  $\text{CH}_4$  oxidation has not yet been quantified as clearly. Because this plays an important role in the relationship between  $[\text{OH}]_{GM}$  and the atmospheric oxidizing efficiency, as discussed above, we do this here. In Fig. 4 we show the breakdown of the percentage of oxidation of  $\text{CH}_4$  which occurs in subdomains of the atmosphere based on the OH distributions considered here. Figure 5 gives an overall impression of this breakdown as the average of the values for all four OH distributions in Fig. 4 taken over larger subdomains, along with the same summary information for  $\text{CH}_3\text{CCl}_3$ .

The values in Fig. 4 are a reflection of the OH distributions in Fig. 1 and the temperature distribution in the atmosphere (along with the slight asymmetry in  $\text{CH}_4$ , with  $\sim 10\%$

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more in the NH). We find that in the extratropics ( $30^{\circ}$ – $90^{\circ}$ ), more is oxidized in the NH than in the SH in all four of the distributions. The OH-S distribution yields an opposite asymmetry in the tropics, so that on the whole the amount of  $\text{CH}_4$  oxidation (and the OH amounts) based on OH-S is roughly hemispherically symmetric; however, this results from the balance between the opposing asymmetries in the tropics and extratropics. The MATCH OH distributions, on the other hand, favor the NH in both the tropics and the extratropics. The north-south asymmetry has been discussed in several studies; often model results, such as those shown here, are in contradiction with observational evidence (e.g. Brenninkmeijer et al., 1992; Montzka et al., 2000). The reasons for this are currently unclear.

The summary in Fig. 5 shows the dominance of the tropical lower troposphere in the overall oxidation of  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$ , where on average  $>60\%$  of the total oxidation occurs. The tropical mid troposphere, and the extratropical lower tropospheres, particularly in the NH, play secondary roles. The upper troposphere and stratosphere combined are responsible for  $<10\%$  of the total oxidation of these gases, and the region above 300 hPa accounts for  $<6\%$  of the total. This indicates that the focus on comparing mean OH concentrations, to the extent that these should be indicative of the global oxidizing efficiency, should be on the lower and mid troposphere, particularly in the tropics.

## 7. Atmospheric subdomains for comparing OH distributions

Figure 4 can be used to help devise a strategy for comparing modeled OH distributions. This should be a balance between: (1) sufficient information to really judge whether OH distributions are similar, at least in terms of their role in determining the atmospheric oxidizing efficiency; (2) manageability of the amount of numbers to compare, and (3) applicability to various model settings. In this regard, a generic parameter (mass or volume weighted  $[\text{OH}]$ ), rather than one tied to a specific gas (e.g.  $\text{CH}_4$ ), would be desirable, since it would make the comparison less dependent on model parameters

such as the temperature and trace gas distributions. However, as found above, this is not reasonable on a global basis, so that a breakdown into atmospheric subdomains needs to be considered.

5 In the previous section it was shown that the vast majority ( $\sim 95\%$ ) of the  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  oxidation occurs in the region below 300 hPa. This region is also favorable for comparing models, since it is (nearly) always within the troposphere, and most models have significant uncertainties in the vicinity of the tropopause. Furthermore, some models have upper boundaries around 100 hPa, which can introduce further uncertainty in the uppermost model layers due to the proximity of nearby boundary conditions. Thus we suggest that the regions to be used for comparing OH can be limited to domains below 300 hPa; studies which are interested in the OH concentrations above this level are generally focusing on issues besides the atmospheric oxidizing efficiency.

10 A sensible horizontal breakdown of the troposphere is into the tropics and extratropics, which captures the major differences in OH levels and regional temperatures. Here we have used the same breakdown as in (Prinn et al., 1995, 2001). As shown above, this is sufficient to discern the character of any north-south asymmetry, such as discussed above for OH-S and the MATCH-MPIC OH distributions.

20 Based on the features of the OH distributions in Fig. 1, and the generally large ( $\sim 30^\circ\text{C}$ ) difference in temperature at the surface and the mid troposphere, we have broken down the troposphere into three vertical subdivisions below 300 hPa. In particular, the importance of the vertical division at 800 hPa can be seen by comparing the OH-S results with the OH-2 results. While the OH-S distribution leads to over 50% more  $\text{CH}_4$  oxidation in the lower free troposphere (800–500 hPa) than in the boundary layer (surface–800 hPa), the OH-2 distribution results in nearly even amounts of oxidation in the two vertical domains. In this case, it would be clearly possible for the two distributions to have similar mass- or volume-weighted mean OH concentrations in the larger region between the surface and 500 hPa, but very different oxidizing efficiencies with respect to  $\text{CH}_4$ .

25 Thus we recommend that comparisons of the mass weighted regional mean OH

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concentrations ( $[\text{OH}]_{RM}$ ) be broken down into 12 subdomains, with vertical divisions at 800 and 500 hPa and a top at 300 hPa, and horizontal divisions at 30° S, 0°, and 30° N. Since the extratropical upper troposphere (30°–90°, 500–300 hPa) contributes very little to the overall atmospheric oxidizing efficiency, one could reduce the total

5 number of subdomains to 10 by leaving these two regions out.

For each of the 12 subdomains suggested here, the relationship between  $[\text{OH}]_{RM}(\text{M})$  and  $[\text{OH}]_{RM}(\text{CH}_4)$  (or  $\tau(\text{CH}_4)$ ) is relatively constant. In comparison to the spread of >10% seen in Fig. 2b, the mean spread in the ratio of  $[\text{OH}]_{RM}(\text{M})/[\text{OH}]_{RM}(\text{CH}_4)$  for these 12 regions is 2.6%, with a standard deviation of 0.7%. The spread for the volume weighted regional means ( $[\text{OH}]_{RM}(\text{V})/[\text{OH}]_{RM}(\text{CH}_4)$ ) is somewhat worse, averaging  $3.6 \pm 0.7\%$ . Thus, the  $[\text{OH}]_{RM}(\text{M})$  (and  $[\text{OH}]_{RM}(\text{V})$ ) values broken down into these regions are relatively representative of the oxidizing efficiency of each region, and should provide an appropriate test of modeled OH distributions.

## 8. Conclusions and recommendations

15 What does the global mean OH concentration tell us about the oxidizing efficiency of the atmosphere? We have shown in this study that the answer to this depends critically on the weighting which is used to compute this value, as well as the domain over which it is integrated. We found that differences in  $[\text{OH}]_{GM}$  can be as large as 30% due to employing different weightings which have historically been used, and >10% for different domains. These numbers are comparable to the stated uncertainty in  $[\text{OH}]_{GM}$  (e.g. Prinn et al., 2001; Spivakovsky et al., 2000; Krol et al., 1998). They are also significant in light of the consideration that all but a few of the values in Tables 1 and 2 lie within about 50% of each other (range 0.75–1.25 molec/cm<sup>3</sup>). Since widely varying studies tend to give  $[\text{OH}]_{GM}$  values which lie within this relatively limited range, a meaningful comparison between  $[\text{OH}]_{GM}$  from different studies can only be done with similarly-computed values. Otherwise it is difficult to determine whether the agreement in  $[\text{OH}]_{GM}$  from different studies is coincidental or real. The same principle also applies

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to trends in  $[\text{OH}]_{GM}$ . For example, consider the scenario in which the total number of OH molecules increases by a certain amount (say 1%/yr). This would lead to the same trend in the volume-weighted  $[\text{OH}]_{GM}$  value, regardless of whether the increase occurs in the upper troposphere or near the surface. However, the same increase would cause a larger trend in mass-weighted  $[\text{OH}]_{GM}$  if it occurred near the surface than if it occurred higher up. Whether or not this may help to explain any of the difference in the OH trends in (Krol et al., 1998) and (Prinn et al., 1995, 2001), which used volume,  $\text{CH}_3\text{CCl}_3$  mass, and air mass weighting to compute  $[\text{OH}]_{GM}$ , respectively, remains to be determined.

In this study we have focused on how to compare OH distributions in light of their ability to serve as indicators of the global oxidizing efficiency, where the oxidizing efficiency with respect to a given gas X is defined as the inverse turnover time of X. We showed that  $[\text{OH}]_{GM}$  is a direct indicator of the oxidizing efficiency with respect to a gas X only when it is weighted by the reaction with X ( $[\text{OH}]_{GM}(\text{X})$ ), in which case it is inversely proportional to the turnover time of X, with the proportionality coefficient dependent only on the domain of integration and the reaction rate coefficient. In contrast to this, on a global basis neither the mass-weighted nor the volume-weighted  $[\text{OH}]_{GM}$  values are very good indicators of the atmospheric oxidizing efficiency, since they are not sensitive to the regions where temperatures are highest, and thus where oxidation reactions are fastest. However, when the atmosphere is broken down into smaller domains, over which  $[\text{OH}]$  and the temperature vary less significantly, then it was shown that  $[\text{OH}]_{RM}(\text{M})$  (and to an extent  $[\text{OH}]_{RM}(\text{V})$ ) can also serve as good indicators of the regional oxidizing efficiency.

The findings in this study lead us to the following recommendations for future studies:

1. Global mean OH should be computed by weighting with the reaction with  $\text{CH}_4$  (Eq. 2), since this provides a direct indication of the atmospheric oxidizing efficiency with respect to the most important greenhouse gas which is mainly removed by reaction with OH, and since it is rather insensitive to differences in the vertical extent of the tropospheric domain used in its computation;

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2. The tropospheric turnover time of  $\text{CH}_4$  ( $\tau(\text{CH}_4)$ ) should be provided as an additional parameter indicating the oxidizing efficiency (with respect to  $\text{CH}_4$ ) related to a particular OH distribution; however,  $\tau(\text{CH}_4)$  is rather sensitive to the domain of integration, and it is unclear at present whether the atmospheric research community is best served by the value integrated up to some pressure level (e.g. 200 hPa) or a climatological tropopause;
3. Serious evaluations of modeled OH distributions should break down the OH distribution into regional mean mass weighted values ( $[\text{OH}]_{RM}(\text{M})$ ) in tropospheric subdomains, in particular the 12 which have been discussed here; alternatively, the two extratropical upper tropospheric domains could be neglected for the sake of the tropospheric oxidizing efficiency to bring the total down to 10. For future comparisons, the  $[\text{OH}]_{RM}(\text{M})$  values in each of these 12 subdomains for the four OH distributions considered here are given in Table 4.

The first two recommendations imply that we see little sense in providing values of  $[\text{OH}]_{GM}(\text{M})$  or  $[\text{OH}]_{GM}(\text{V})$  in future studies for the sake of indicating the atmospheric oxidizing efficiency (as defined here), or for comparing modeled OH fields. Nevertheless, it is certainly possible that other uses will be found for these parameters beyond the two limited purposes considered here (oxidizing efficiency and model comparisons).

The third recommendation is clearly a difficult one to adopt on a widespread basis, since it is generally desirable to have a single number, where possible, which indicates model performance. However, we feel it is critical that the distribution of OH be taken into consideration in this or a similar way in future studies. Concluding that a model simulation of OH is “reasonable” because the global mean OH concentration is in good agreement with that from another study can be misleading, since two OH distributions can readily have the same  $[\text{OH}]_{GM}$  values computed using different weightings, but very different distributions (e.g. one more concentrated towards the surface than the other), which would result in different oxidizing efficiencies. Although we do not wish to single out any particular studies here, we have found several instances in the literature

in which such comparisons of differently computed  $[\text{OH}]_{GM}$  values have been made (in some cases inadvertently, due to misinterpretation of other studies where the weighting which was used was unclear).

Our proposal for a single number which indicates the degree of agreement between various OH fields, both in terms of their amounts and their distributions, is the RMS deviation between  $[\text{OH}]_{RM}(M)$  in the 12 subdomains depicted in Table 4. For the MATCH-MPIC OH distributions relative to the OH-S distribution, these values are (in  $10^6 \text{ molec/cm}^3$ ): 0.22 (OH-1), 0.35 (OH-2), and 0.32 (OH-3). When considered in light of the global mean values of order  $1 \times 10^6 \text{ molec/cm}^3$ , these RMS differences are relatively high; they are nearly twice as large as the mean deviations based on the global values in Table 2 (0.11, 0.26, and 0.17, respectively). Thus since our proposed approach is sensitive to both the OH amounts and its distribution (particularly the differences in the tropical vertical distributions seen in Fig. 1), it is thus much more informative (than simply comparing global means) about the degree to which various OH distributions agree or disagree.

We offer these recommendations as a starting point for discussion by the community, and are open to suggestions of alternate approaches to those proposed here. There are a number of related issues which are in particular need of further consideration. First, we have only briefly mentioned the temporal averaging here. Properly, one would compute  $[\text{OH}]_{GM}$  using the  $[\text{OH}]$ , temperature, pressure, and trace gas (e.g.  $\text{CH}_4$ ) fields for each model timestep, so that particularly the correlation between diurnal variations in  $[\text{OH}]$  and temperature are captured. However, for model output at high spatial resolution like that considered here, this is beyond the storage capacity of many computing environments, so instead we have employed monthly-mean values. We expect this to be a minor effect in light of the many other uncertainties, but this nevertheless needs to be carefully assessed in a future study. Another point which will need to be considered is how to handle updates in the rate coefficients of OH with  $\text{CH}_4$  and other gases, which affects the turnover time and the  $[\text{OH}]_{GM}(X)$  values computed based on a given OH distribution. Finally, we recommend that the atmospheric

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research community develop clear, broadly accepted definitions of the terms “oxidizing efficiency”, “oxidizing power”, “oxidizing capability”, and “oxidizing capacity”; various definitions have been used in the past (e.g. [Thompson, 1992](#)), and a working definition of the oxidizing efficiency has been proposed here.

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**Table 1.** Survey of recent published values of  $[\text{OH}]_{GM}$  ( $\times 10^6$  molec/cm<sup>3</sup>)

Reference	$[\text{OH}]_{GM}$	Weighting <sup>a</sup>	Domain
(Spivakovsky et al., 1990)	0.8	Mass	below 100 hPa
(Prather and Spivakovsky, 1990) <sup>b</sup>	0.8	Mass	below 100 hPa
	0.65	Volume	
	1.05	CH <sub>4</sub>	
	1.06	MCF	
(Crutzen and Zimmermann, 1991)	0.7	Mass <sup>c</sup>	below 100 hPa
(Hough, 1991)	0.83	?	troposphere <sup>d</sup>
(Prinn et al., 1995)	0.97 ( $\pm 0.06$ )	MCF-Mass <sup>c,e</sup>	below 200 hPa
(Derwent, 1996)	1.2	?	0–12 km
(Berntsen and Isaksen, 1997)	1.1	Volume <sup>f</sup>	below $\sigma = 0.152$
(Collins et al., 1997)	1.4 <sup>g</sup>	Volume	below $\sim 89$ hPa <sup>h</sup>
(Hein et al., 1997)	1.03	MCF	troposphere <sup>i</sup>
(Krol et al., 1998) <sup>j</sup>	1.07 <sup>+0.09</sup> <sub>-0.17</sub>	Volume <sup>c</sup>	below 100 hPa
(Wang et al., 1998)	1.0	Mass	below 200 hPa
	1.2	MCF	
(Karlsdottir and Isaksen, 2000)	1.01 <sup>k</sup>	?	?
(Montzka et al., 2000)	1.1 ( $\pm 0.2$ )	MCF	below $\sim 180$ hPa <sup>l</sup>
(Poisson et al., 2000) <sup>m</sup>	1.24	Mass	below 100 hPa
	1.56	CH <sub>4</sub>	
(Roelofs and Lelieveld, 2000)	1.00 <sup>n</sup>	Volume <sup>c</sup>	troposphere <sup>o</sup>
(Spivakovsky et al., 2000)	1.16 ( $\pm 0.17$ ) <sup>p</sup>	Mass	0–32° lat: below 100 hPa; >32° lat: below 200 hPa
(Prinn et al., 2001)	0.94 $\pm$ 0.13	Mass <sup>q</sup>	below 200 hPa
(Wang et al., 2001)	0.9	?	?

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<sup>a</sup> “Volume” and “Mass” imply weighting by the atmospheric volume or air mass (or density), “CH<sub>4</sub>” and “MCF” imply weighting by the product of their mass and reaction rate with OH (Eq. 1 and 2)

<sup>b</sup> Based on the same OH distribution as in (Spivakovsky et al., 1990); the CH<sub>4</sub> and MCF reaction weighted values assume a uniform distribution for these two gases; values were also given for hypothetical gases with temperature dependences of  $\exp(-1000/T)$  and  $\exp(-2300/T)$  in their reaction rate coefficients with OH, yielding  $[\text{OH}]_{GM}$  values of  $0.96$  and  $1.11 \times 10^6 \text{ molec/cm}^3$ , respectively

<sup>c</sup> Based on Personal Communication (not stated explicitly in the original publication)

<sup>d</sup> Not clearly defined

<sup>e</sup> Weighted only by CH<sub>3</sub>CCl<sub>3</sub> mass, not the reaction rate; in the paper this was referred to as the “temperature and atmospheric density-weighted average”

<sup>f</sup> Called the “arithmetic mean”, presumed to imply volume weighted

<sup>g</sup> Mean of the values given for Feb. (1.39) and Aug. (1.41)

<sup>h</sup> Below hybrid coordinate level  $\eta = 0.1$

<sup>i</sup> Tropics: below model level centered at 200 hPa, Extratropics: below model level centered at 320 hPa

<sup>j</sup> Values for 1993 given here; 1978 value was  $1.00^{+0.09}_{-0.15}$

<sup>k</sup> 1996 value taken from their Fig. 2, ranges from 0.95 in 1980 to 1.01 in 1996

<sup>l</sup> The tropospheric mass is assumed to be 0.82 of the total atmospheric mass, implying an upper bound of approximately 180 hPa

<sup>m</sup> Values with NMHCs given here, without NMHCs the values were 1.45 and 1.81, respectively

<sup>n</sup> Value with NMHCs given here, without NMHCs it was 1.08

<sup>o</sup> Defined based on thresholds for the potential vorticity and lapse rate

<sup>p</sup> Range based on the maximum uncertainty estimate of 15%

<sup>q</sup> Nearly the same value (0.93) was found for the CH<sub>3</sub>CCl<sub>3</sub> mass-weighted (not reaction-weighted) mean OH concentration

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**Table 2.** Global annual mean OH levels ( $\times 10^6$  molec/cm<sup>3</sup>) for different OH distributions and weightings

Weighting Factor	OH-S	OH-1	OH-2	OH-3
Air Mass	1.14	1.26	0.88	0.95
Air Volume	1.10	1.28	0.82	0.87
CH <sub>4</sub> Reaction	1.32	1.39	1.06	1.19
CH <sub>3</sub> CCl <sub>3</sub> Reaction	1.29	1.38	1.04	1.16

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**Table 3.** Global annual mean turnover times (years) for CH<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub>

Gas	OH-S	OH-1	OH-2	OH-3
CH <sub>4</sub>	8.23	7.79	10.25	9.12
CH <sub>3</sub> CCl <sub>3</sub>	4.95	4.66	6.16	5.50

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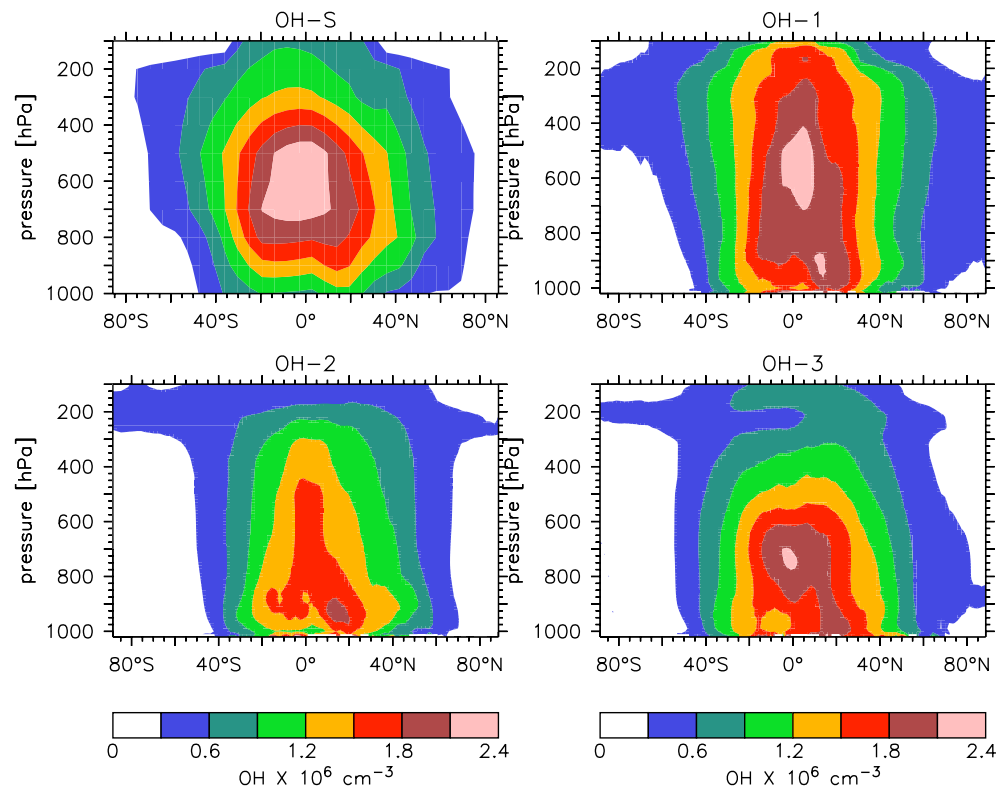
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**Table 4.** Regional annual mean mass-weighted OH levels ( $\times 10^6$  molec/cm<sup>3</sup>) for different OH distributions in the recommended subdomains

Region	OH-S	OH-1	OH-2	OH-2
Below 800 hPa, 90°S–30°S	0.44	0.43	0.35	0.51
Below 800 hPa, 30°S–0°	1.33	1.55	1.31	1.48
Below 800 hPa, 0°–30°N	1.43	1.86	1.54	1.74
Below 800 hPa, 30°N–90°N	0.72	0.86	0.81	0.86
800 - 500 hPa, 90°S–30°S	0.70	0.54	0.36	0.47
800 - 500 hPa, 30°S–0°	1.97	1.65	1.20	1.51
800 - 500 hPa, 0°–30°N	1.97	1.92	1.38	1.65
800 - 500 hPa, 30°N–90°N	0.88	0.90	0.66	0.74
500 - 300 hPa, 90°S–30°S	0.65	0.64	0.35	0.35
500 - 300 hPa, 30°S–0°	1.52	1.58	1.09	0.88
500 - 300 hPa, 0°–30°N	1.46	1.79	1.20	1.03
500 - 300 hPa, 30°N–90°N	0.67	0.96	0.59	0.53

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**Fig. 1.** The annual zonal mean OH fields based on the four distributions considered here: **(a)** OH-S (Spivakovsky et al., 2000); **(b)** OH-1 (Lawrence, 1996); **(c)** OH-2 (Lawrence et al., 1999); and **(d)** OH-3 (von Kuhlmann, 2001). The zonal mean values are computed by weighting every grid cell around a latitude band evenly, which is default for our plotting programs, and presumably for most others. Note, however, that the same arguments discussed in the text apply here: different plots could be produced by computing the zonal OH levels differently, e.g. weighting by the reaction with  $\text{CH}_4$ .

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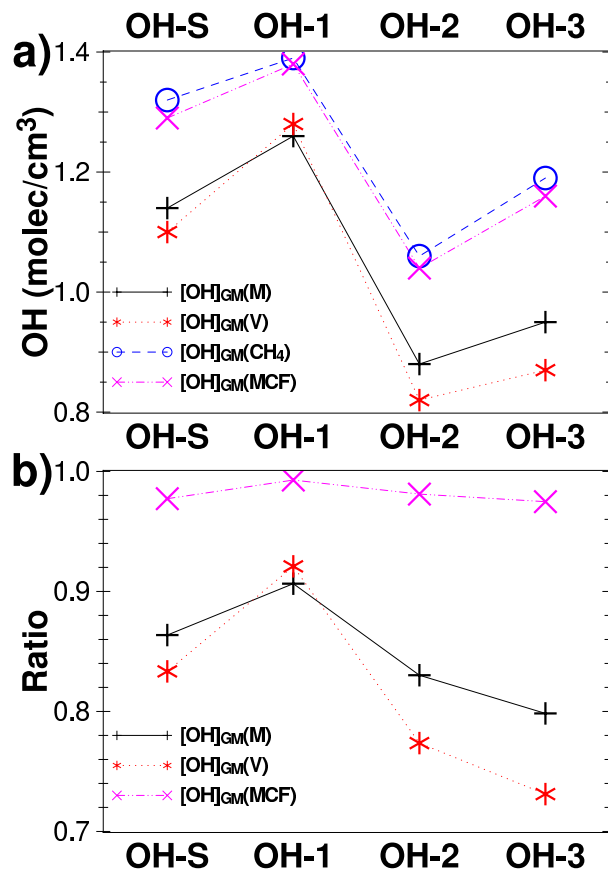
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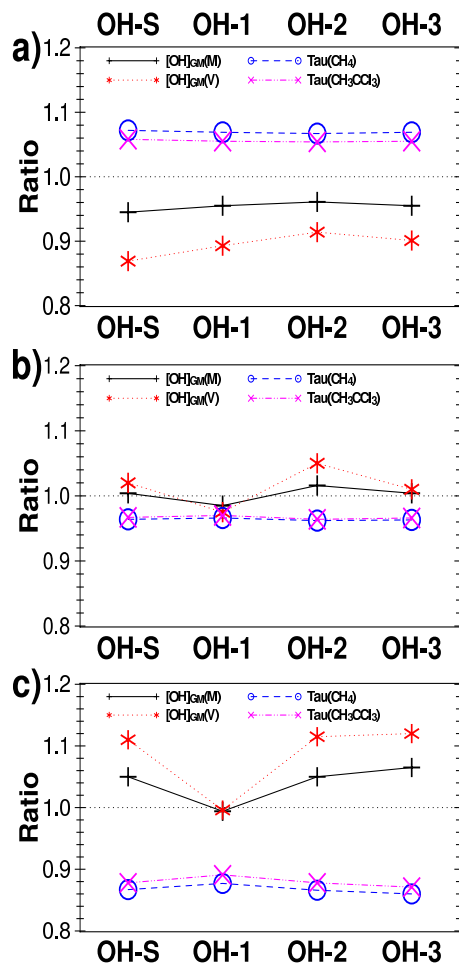
**Fig. 2.** Depictions of the relationships between different ways of computing the tropospheric  $[\text{OH}]_{\text{GM}}$ : **(a)**  $[\text{OH}]_{\text{GM}}$  values for the four distributions and four weightings discussed in the text; **(b)** ratio of  $[\text{OH}]_{\text{GM}}$  values for three weightings versus  $[\text{OH}]_{\text{GM}}(\text{CH}_4)$ .

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**Fig. 3.** The ratios of  $[\text{OH}]_{\text{GM}}(\text{M})$ ,  $[\text{OH}]_{\text{GM}}(\text{V})$ ,  $\tau(\text{CH}_4)$ , and  $\tau(\text{CH}_3\text{CCl}_3)$  for **(a)** the domain below 100 hPa, **(b)** the domain below 200 hPa, and **(c)** the domain below 300 hPa, versus the values for the climatological troposphere (Eq. 6).

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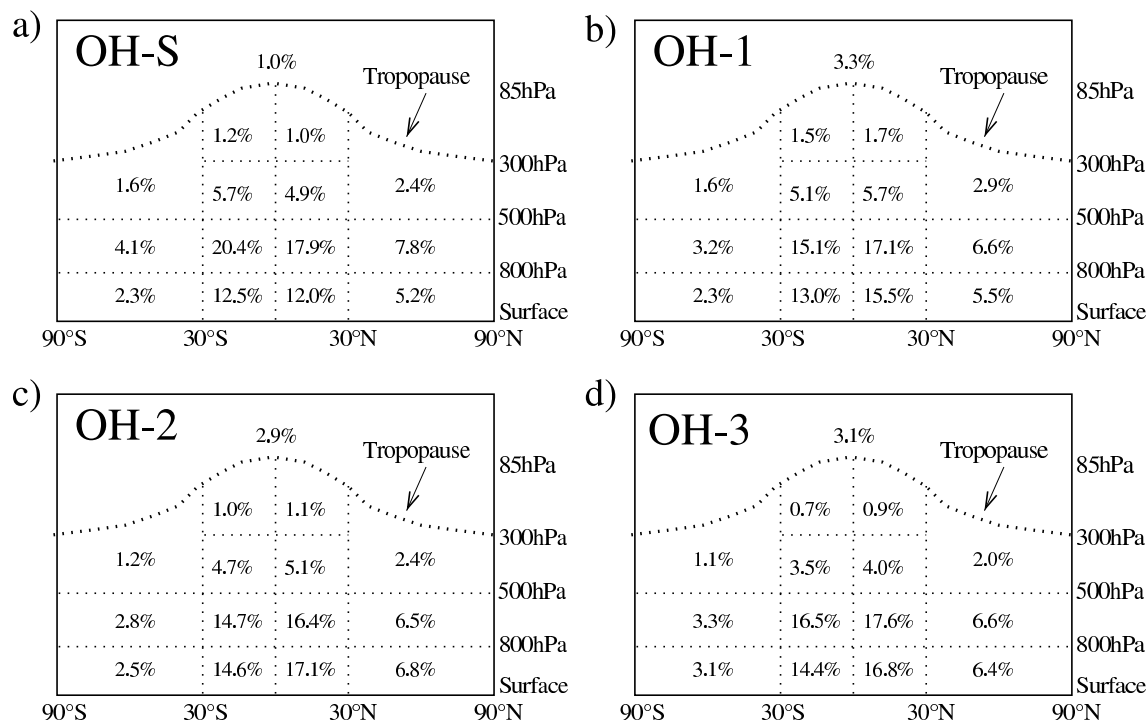
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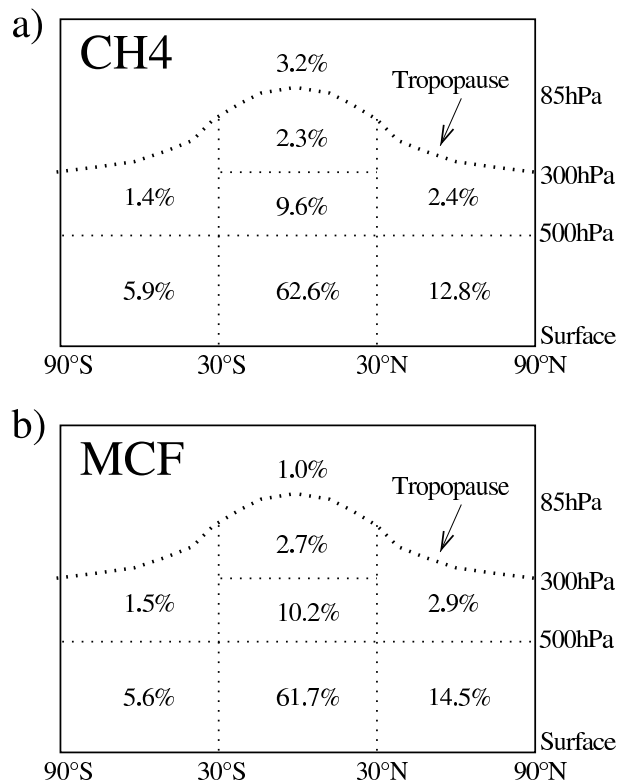
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**Fig. 4.** The percentages of  $\text{CH}_4$  which are oxidized in various subdomains of the atmosphere based on four different OH distributions: **(a)** OH-S; **(b)** OH-1; **(c)** OH-2; **(d)** OH-3.

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**Fig. 5.** The percentages of (a) CH<sub>4</sub> and (b) CH<sub>3</sub>CCl<sub>3</sub> which are oxidized in various subdomains of the atmosphere based on the average of the four OH distributions (OH-S, OH-1, OH-2, and OH-3). Numbers may not add up exactly to 100% due to roundoff.

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